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A chemiluminescence method of measuring ozone in the atmosphere was suggested by Regener [1, 2], who has enjoyed wide application of his techniques. In this work is a description of the methods of preparing chemiluminescent materials using Regener's technique involving the use of domestic Rhodamine <sup>C</sup>, luminescence spectrum of this material and results of preliminary photoelectric measurements.

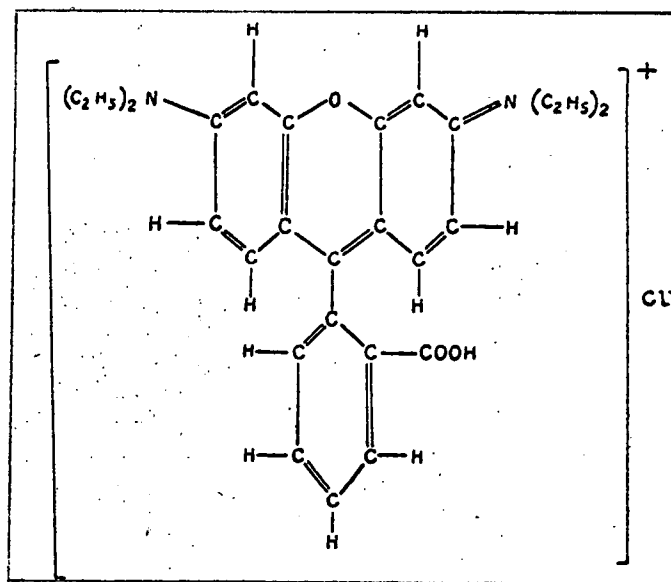
Regener's Technique: To prepare luminous material, finely ground silica gel and an aqueous solution of Rhodamine <sup>B</sup> is necessary (2 g for 1 l.). The silica gel is mixed with Rhodamine <sup>B</sup> until a thick, paste-like mass is formed, which is dried in air at a temperature of +100° C. The drying process is then continued in an air-tight furnace at a temperature of +200° C. Into the resultant powder is added an aqueous solution (30 g for 1 l.) of mucilage--gum arabic and this forms another thick, pasty mass. The drying process is repeated. If the last drying phase in the air-tight furnace is conducted for a period of 20 hours at a 220° C temperature, then according to Regener, the material becomes more stable to prolonged ozone action. However, it loses some of its sensitivity.

According to [2], the addition of mucilage increases the sensitivity of the chemiluminescing material to ozone by 50 times. In

Regener's prescription, there is, unfortunately, no accurate data concerning the duration period which is mandatory for drying-out (with the exception of the last stage). No degree or vacuum is indicated and also remaining unclear is the condition of the resultant material utilized in the apparatus. In [2], there is no indication of the spectral region of chemiluminescent light.

Rhodamines. These are powder like crystalline materials belonging by chemical structure, to xanthene coloring material and by technical properties to a group of basic coloring materials. There are several brands of Rhodamines. Rhodamine <sup>B</sup>~~S~~, used by Regener, corresponds to Rhodamine <sup>C</sup>~~S~~ ( $C_{28}H_{31}O_3N_2Cl$ ), which is produced by our commercial plants for technical purposes. The structural formulas of indicated Rhodamine brands, according to [3] and [4], coincide (Fig. 1):

Figure 1. Structural formula of Rhodamine <sup>C</sup>~~S~~ [4].



However, by exterior looks, they slightly differ. Rhodamine S has a more finely structured powder than Rhodamine <sup>B</sup>~~S~~, and a slightly different colored hue possibly due to the technology processes.

Silica gel. Silica gel are well known as effective adsorbers. They actively absorb moisture until the ashes of  $\text{SiO}_2$  particles are no longer surrounded by a tight hydrate shell, obstructing the process of further adsorption. When these ash-particles are baked, they are released from the hydrate shell and the adsorption capability is resumed [1]. The baking temperature needed depends on the brand of silica gel. Large-pore silica gel, according to [5], is baked at  $110^\circ \text{C}$  while fine-pore is baked at  $170 - 180^\circ \text{C}$ . In our work a brand with a large capacity of adsorption was used, a thermo-stable, fine-pore silica gel of KSM brand.

Vacuum installation. The exterior view of the vacuum installation utilized in this experiment is shown in Fig. 2. The glass cover (1), situated on a tripod (2), connected to preliminary vacuum pump. Under the glass cover is an electric heater (3), which is made from mica wound around with a mixed-chrome wire. The porcelain cup with the powder is placed on the tripod (A) in such a manner as not to bring it in contact with the surface of the heater.

The temperature of the powder in the cup was measured by a thermocouple (copper-constantan) connected to a multivolt meter. Temperature regulation was effected with the aid of a rheostat.

The measurement of the vacuum was made with a thermocouplc vacuumeter, the type of VIT-IAU. The preliminary vacuum pump insured a vacuum of  $3 \cdot 10^{-2}$  mm col. merc.

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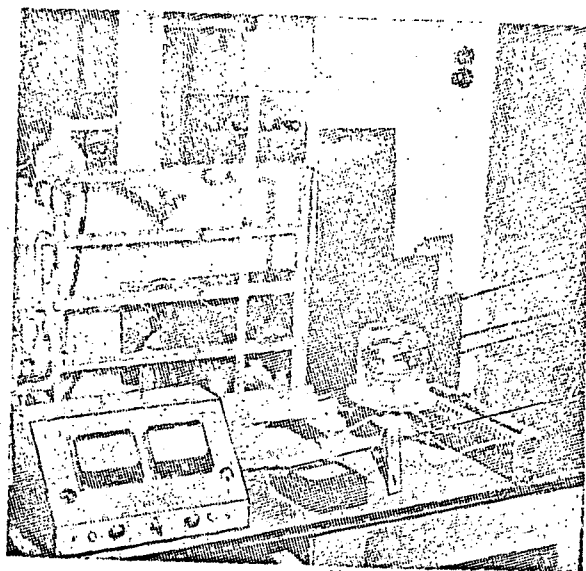


Figure 2. Exterior view of the vacuum installation.

Preparation of active powders. In preparing these powders, we utilized Regener's techniques. Silica gel KSM was baked for a period of 4 - 5 hours in a drier at a 180 - 170° C temperature. Then this was thoroughly refined and mixed with an aqueous solution of Rhodamine <sup>C</sup> until formation of a paste-like mass (according to Regener). The resultant mass was dried in air for a period of time (approximately 45 min.) at +100° C, then again in the drier at the same temperature for 2 - 3 hours. During the first 45 minutes of drying, the moisture separation process is very intensive and resembles vigorous boiling. The entire drying process was conducted with stirring the mass, in order not to singe the lower layer. The paste-like mass took on a powder-like appearance and a pink-raspberry color. The duration of the open method drying depended on the amount of the mass to be dried. The absence of moisture on the glass cover after having switched on the vacuum pump is the criterion in this case. After reaching this criteria, the drying process is continued in the vacuum at a temperature of approximately +200° C. It should be noted that we had no means of stirring the powder in the vacuum which negatively affected our experiments since the heating temperature was not identical for the whole mass. The lower layer of the powder was singed during the prolonged drying.

An aqueous solution of gum arabic was added into the powder dried in this manner. This was continued until a paste-like mass was formed. Then the described drying process was repeated. The

drying time period in the vacuum with the glue and without it was changed from 1 to 20 hours for the determination optimal conditions. After the drying process, the examined mixture again reverted to a powder-like form. Distilled water was used to obtain the necessary solutions. The gum arabic was dissolved in warm water. The powders obtained with various processing methods was examined under lumin-  
excence with ozone action. Ozone was produced in the ozonizer by electrical discharge from oxygen in the air. The ozonized stream, assisted by an air pump was directed into the material being examined. The luminexcence was well noticed in a darkened room by the adapting eye when the ozonized air stream directly touched the powder surface.

Luminescence spectrum of the powder. For the recording of these spectrum, a spectrograph with a glass lens was utilized, light aperture of  $1 \cdot 4.3$  and a dispersion in the yellow-red region of  $300 \text{ \AA/mm}$ . After preliminary experiments, which allowed determination of the approximate luminescence region, for the recording of the spectrum a photofilm type "E" was selected. For spectrum comparison, the spectrum of a neon lamp was used. In fig. 3 is shown a micro-  
photogram of neon spectrum and chemiluminescence illumination, obtained with a 0.6 mm aperture and a 2 hour exposure. From fig. 3, it can be seen that the luminescence consists of a broad, un-  
structured band in the red-yellow region of the spectrum.

In the process of this work it became clear that chemilumin-  
escent powder with a continuous action of an ozonized air stream

rapidly scintillated, and the powder color changed--it whitened. For 2 hour exposures it was necessary to change the powder with fresh samples, which was visually determined very well.

The obtained chemiluminescence region of Rhodamine S which was absorbed by silica gel compares white well with data of Kautsky and Neitzke. [6]

Photoelectric measurements. Preliminary photoelectric measurements were made to explain certain technological preparations and temporary luminescent characteristics. To assist in this, a photon-multiplier was fastened over the cup with the chemiluminescent powder. To avoid other luminescence, a special tube with side branches through which ozonized air passed was constructed. A connection to the photon housing was made and the powder in the cup was covered.

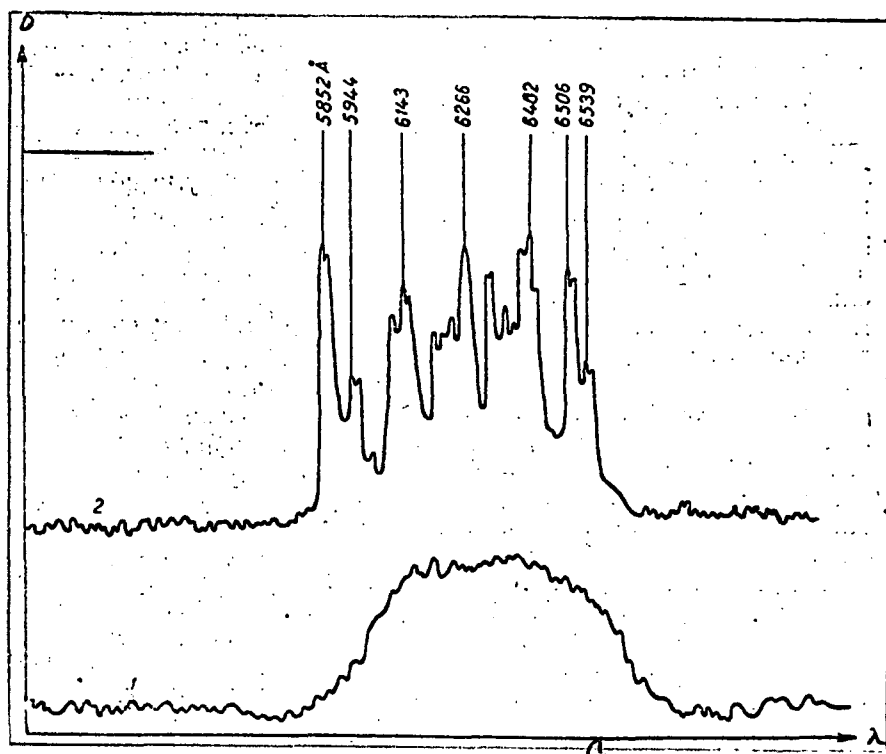


Figure 3. Microphotogram of Rhodamine and neon spectrum.  $D$ --darkening density, ul. unit. 1--Rhodamine spectrum. 2--neon spectrum.

The photon (FEU--38) utilized in this work had a multi-alkali cathode with a maximum sensitivity in the 5000 - 6000 Å region. The FEU signal emerged with the chemuliminescence of the powder, was transmitted to the D.C. current amplifier, with an amplification coefficient of  $3 \cdot 10^2$  and was then registered by a microampere-meter.

The first experiments showed that with ozone concentrations, obtained by our ozonizer (they are approximately  $10^4$  times larger than natural ones) a relatively strong but unstable luminescence was discovered. This was to be expected after experiments of spectrum recording. With given parameters of photoelectric schematics, we obtained signals of 30 to 150 microamperes.

The process characteristics of luminescence with introduction of ozonized air over the powder surface is similar to luminol luminescence described by Bernanose and Rene [7]. After 1 - 2 sec. exposure of the ozonized stream in the powder, there emerges a strong luminescence (130 - 150 m.a.) decreasing over a period of time (in 30 min. to 10 m.a.). The initial brightness depended, other conditions being equal, on the powder temperature itself.

The lack of correspondence of our data with that of Regener's [27] can probably be explained by the excessively high concentrations of ozone formed by our ozonizer.

Analyzing the relationship between the initial luminescence brightness and powder preparation methods, we came to the conclusion that luminescence brightness depends on the heating temperature in

the vacuum heater as well as duration of drying in the vacuum. The following conditions proved to be more effective: temperature 160 - 180° C, first drying process in vacuum 15 hours, second one 20 hours (after addition of gum arabic). Under these conditions a more stable and bright luminescence was achieved. In our experiments, the addition of gum arabic resulted only in stability increase and not in brightness. Stability in this case was determined by the capability of the powder to chemiluminescence after 5 days of the preparation with the same initial brightness as in the first day (at room temperature).

In this way, during the first experiments only the possibility of using native brand Rhodamine S for chemiluminescent reactions with ozone and determining the spectral region of this luminescence, caused a limiting factor. For further verification of these conclusions, all experiments were duplicated with Rhodamine V (imported). Very little differentiation was noted between the two products.

Nature of chemiluminescence process. The basic difficulty in exploring chemiluminescence was that not in any instance in the many experiments was there a means of determining accurately, which intermediate reactions and components were responsible for radiation. This was true even when the experiments were conducted with structures of materials that were well known [8, 9]. The problem is further complicated by the fact that occasionally materials of the same class, having analogous structures and with the same conditions, give completely different luminescent intensity [10]. Besides that, until recently, most chemiluminescence reactions were investigated qualitatively, due to a lack of reliable experimental techniques.

During the past few years, due to a development of photo-electric methods, the possibility of quantitative studies of these manifestations by using photon counters and photomultipliers [12]. However, it is still difficult to ascertain the connection between the known materials chemiluminescence in various physical conditions. It is also difficult to classify known reactions and make conclusions of a general order concerning the luminescence mechanisms [13].

A series of well known materials capable of chemiluminescence are a group of hydrazides [8, 9, 13]. Hydrazides are metallic or acid formations of hydrazine  $N_2H_4$  [14]. Luminol (3--aminophtalic hydrazide) which belongs to this group of materials was used in the first examples of chemiluminescent ozone-probes. On the basis of experiments conducted by various researchers, it was established that chemiluminescence of hydrazides depends on the chemical structure of the material. For example, cyclic hydrazides which are products of phtalic and dicarboxylic acid (which possess characteristic structures of hydrazide rings) give a stronger luminescence [9, 15].

Many hypothesis were expressed concerning the luminescence mechanism [8-10, 13, 16]. Judging by data in literature, the most reliable one which concerns experiments [12, 16 - 18] is the Drew hypothesis [9]. The essence of this is that chemiluminescence process is connected with the formation of hydrazide peroxide and with further formations of these peroxides. The initial stage of luminescence is connected with peroxide ion formation when the double bond of hydrazide rings is broken. In excess conditions of the

oxidized molecules, the peroxide ions are transformed into an unstable, agitated component which rapidly regenerates into the peroxide ion condition and radiates light. According to Drew, this act is basic to chemiluminescence. It is interesting to note that Drew, as well as Gleu and Petsch [10] underscored that the chemiluminescence process in the pure state should not be accompanied by molecular destruction of the basic material [16]. The destruction of molecules is connected with secondary processes. This could be avoided in ideal situations. All existing hypothesis concerning the chemiluminescence mechanisms, even of simple compounds as hydrazides rest on a series of assumptions, any one of which may be incorrect as could be proven by experimental checking. This is stated by the authors, themselves. However, the presence of ion peroxides in chemiluminescent organic material solutions are firmly established experimental facts [9, 12].

It should be noted that all the above mentioned experiments are conducted with chemiluminescence examined in solutions, mainly in alkali ones. In an attempt to classify chemiluminescent reactions, it was established that the amount of oxidized materials capable of originating chemiluminescence is limited. These are ozone, peroxide, hydrogen peroxide, potassium permanganate, hypobromide, hypochlorite and certain others. Each one of these oxidizers brings chemiluminescence of certain materials. For example, nitrate dimethyldiacrydil in an alkali solution causes luminescence only under the action of hydrogen peroxide and does not react with other oxidizers [10]. The

number of organic materials chemiluminescent with the action of ozone is large; of the hydrocarbon compounds are benzol, thiophene, a large hydrazide group mentioned above, ethyl alcohol, resorcin and others. According to Bernanose and Rene [7], a brighter luminescence is obtained with luminol and Rhodamine <sup>B</sup> acting with ozone.

As one can judge from published information, chemiluminescence is a subject not yet investigated fully. Numerous facets, influencing luminescence, complicate the matter considerably.

It can be assumed that the chemiluminescence of Rhodamines adsorbed in silica gel, whose structure is even more complicated than the hydrazites, will present a formidable subject of study. No other information, besides the ones given in [2, 6, 7] concerning chemiluminescence of this group of materials was found by us. Nevertheless, Rhodamines are well known for rather strong fluorescence in dye solutions and in many instances is utilized in fluorescent experiments [11, 19].

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